D1

PATENT SPECIFICATION

(11) 1382991

1382991

(21) Application No. 1485/71 (22) Filed 12 Jan. 1971
(23) Complete Specification filed 11 Jan. 1972
(44) Complete Specification published 5 Feb. 1975
(51) INT CL² B01J 8/24 8/34 C07C 120/14 121/32
(52) Index at acceptance
B1F 3A1A
C2C 200 20Y 326 410 412 413 414 415 417 418 41Y 489 62Y 65Y NP

(19) THE PATENT OFFICE LONDON

(54) PROCESS FOR CARRYING OUT CHEMICAL REACTIONS IN A FLUIDISED BED

(71) We, MIKHAIL GAVRILOVITCH SLINKO, a Russian citizen, of Oulitza Voevodskago No. 2, Akademgorodok, Novosibirsk 72, Siberia, Union of Soviet Socialist Republics, and UCB, S.A. of 4 Chaussée de Charleroi, Saint-Gilles-les-Brusselles, Belgium, a body Corporate organised under the laws of Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a process for carrying out chemical reactions in a fluidised bed.

It is known that the fluidisation technique can be used successfully, particularly in the presence of a catalyst, for carrying out chemical reactions in the heterogeneous gas/solid phase, in which the reagents in the gaseous phase are brought into contact with a fluidised bed of finely-divided solid material, usually possessing catalytic properties. Because of the convenience of fluidisation, this technique is widely used in the chemical manufacturing industry and particularly in the petroleum industry.

Nevertheless, great difficulties are sometimes encountered in carrying out this technique when the reactions in question are highly exothermal, because of the delicate problem of correct dissipation of the heat of reaction. It has, in fact, been found that it is often very difficult to keep the temperature within optimum limits, which often constitute a very narrow range, the obtaining of optimum results being conditional upon correct maintenance of temperature. For this reason, it has been proposed to incorporate cooling means in the reaction vessel with the object of promoting the dissipation of the heat released by the reaction. This measure is, however, often found to be inadequate because other factors considerably lower the activity and selectivity of the catalyst in relation to theoretical values, theoretical values being understood to mean not what would be expected from stoichiometry but, more precisely, what is indicated by kinetic data obtained under ideal conditions free from all the disturbances associated with transfers of heat and mass. This drop in activity and selectivity is caused, amongst other factors, by insufficient exchange of mass between the light and dense phases of the catalytic bed, by the existence of heterogeneity in the latter and by the formation and coalescence of gas bubbles of increasing dimensions. Phenomena known, for example, under the names of "by-passing" and "back-mixing", also intervene. "By-passing" is mainly responsible for the drop in activity associated with too rapid a passing of the reagents into the catalysis vessel. In the case of "black-mixing", instead of travelling normally from the inlet to the outlet of the reactor, the reagents and the products return in the rearward direction and consequently have a longer residence time than was intended, with the corollary of more or less considerable destruction of the reagents and particularly of the reaction products, thus entailing a corresponding loss of selectivity. For this reason, it has been proposed that the fluidised bed should contain grids, lattices, horizontal, vertical or oblique bars or tubes baffles and other filling elements, such as Raschig rings, Berl saddles or the like. Although these various means improve the results of fluid catalysis, there is still room for improvement.

It is, therefore, an object of the present invention to provide improvements to fluid catalysis processes in the case of chemical reactions.

According to the present invention, a process is provided for carrying out chemical reactions, comprising passing at least one gaseous reactant through a fluidised bed of catalyst particles in a reactor, said fluidised bed containing a plurality of filling elements therein to promote homogenity of the fluidised bed, and heat exchange means being provided which maintains the temperature of the fluidised bed at a desired value during the process, wherein the filling elements each consist of a

[*Price 33p*]

winding of rigid material, the total volume of rigid material of said windings representing 2 to 12% of the total volume occupied by the said fluidised bed and the said rigid material and the speed of displacement of the gaseous reactant(s) through the fluidised bed in the reactor (as hereinafter defined) as from 0.25 to 0.95 times the speed that would cause the entrainment of the particles of the fluidised bed of catalyst out of the reactor by the gaseous reactant(s). Preferably the total volume of rigid filling material represents from 3 to 10% of the total volume occupied by the fluidised bed and rigid material. Preferably, the speed of displacement of the gaseous reactants through the fluidised bed is 0.40 to 0.90 times the speed which causes the entrainment of the particles of the fluidised bed of catalyst out of the reactor by the gaseous reactant(s).

The speed of displacement of gaseous reactant(s) through a fluidised bed in the reactor is given by the equation $L \times V/V'$, in which L is the length of the fluidised bed, V is the volume of gaseous reactants passing through the fluidised bed per second and V′ is the volume of the fluidised bed. This speed, expressed by the above equation, is a universal one which is independent of any variations of speed in different parts of the bed.

The rigid material of the filling windings may be composed of a material which is inert or catalytically active in relation to the gaseous reagents. It is preferably of a material selected to withstand both the erosion caused by the fluidised catalyst particles and the reaction conditions, for example, temperature and pressure. Therefore, in each particular case, the nature of the material must be adapted to the particular reaction and also to the conditions under which the reaction is carried out; by way of example, there may be used glass, ceramic materials and inert or catalytically-active metals and metal alloys.

In contradistinction to the fine wire lattices previously used as filling elements, the fillings used in the process of the present invention are composed of windings of rigid material, for example wire of a diameter of at least 0.4 mm., so that the windings do not undergo substantial deformation when stacked up on a reactor.

The windings may have their turns separated from one another by a distance which is at least 20 times the dimension of the fluidised catalyst particles, so as to permit free passage of the catalyst particles between the turns of the windings. On the other hand, for a reactor of given dimensions, the dimensions of the windings, i.e. diameter and length, are conveniently such that at least two windings can be placed end to end over the minimum distance separating the walls of the heat exchange means. In addition, the shape of the windings is preferably such that interpenetration is negligible or even impossible. The turns of the windings may be, for example, circular, oval or polygonal.

The fluidised catalyst used in the present process may have the particle dimensions conventionally used in fluid catalysis. In order to obtain optimum results, the granulometry limits of the catalyst particles should be as narrow as possible.

The heat exchange means may be constituted conventionally by tubes or bundles of tubes through which a liquid or gaseous heat exchange fluid passes. Their number and spatial arrangement depend upon the exothermicity or endothermicity of the reaction in question.

The windings may be stacked regularly or irregularly in the zone of the reactor reserved for the catalyst under working conditions, the only requirement being that the volume of material of the windings must constitute from 2 to 12%, preferably from 3 to 10%, of the total volume occupied by the fluidised bed and the rigid material, as has already been indicated above.

In order that the effective heat exchange coefficient of the masses may be high, the fluidisation of the catalyst particles in the reactor containing the windings used according to the present invention should be effected by imparting to the gaseous reactants a speed of displacement through the fluidised bed of from 0.25 to 0.95 times, preferably of from 0.4 to 0.9 times, the speed causing entrainment of the particles of the fluidised bed of catalyst out of the reactor by the gaseous reactants.

The measures proposed according to the present invention considerably reduce "back-mixing" while not reducing axial and radial heat exchange between the fluidised catalyst particles and the walls of the heat exchange means. Furthermore, the homogeneity of the fluidised bed is greatly improved and gas circulation turbulence in the reactor is substantially reduced.

The process of the present invention can be used on an industrial scale. The advantages which it provides includes not only an improvement of the conversion of the gaseous reagents used for the reaction and the efficiency in respect of the desired reaction product but also an increase of the production rate of the reactor because of the high linear gas speeds which are possible in the latter. Furthermore, starting with an experimental reactor, with the windings according to the present invention it is easier to calculate the parameters for a reactor operating on a pilot or industrial scale, which is difficult to do with techniques known at present.

The following Examples of the process of the present invention relate to the synthesis of acrylonitrile from propylene and ammonia. It is, however, to be understood that the pro-

cess of the present invention has a wider scope and is applicable, in principle, to all chemical reactions which can be carried out in a fluidised bed, for example, the catalytic oxidation of naphthalene to phthalic anhydride; of benzene to maleic anhydride; of ethylene and propylene to the corresponding oxides; of ethylene and propylene to acrolein and methacrolein, respectively, or to acrylic or methacrylic acid, respectively; and of isobutene, together with ammonia, to methacrylonitrile; the catalytic dehydrogenation of saturated hydrocarbons into olefins or polyolefins; and the production of chlorine by oxidation of hydrochloric acid.

The catalytic fluidisation reactor used for the tests described in Examples 1 and 2 is made of stainless steel sheeting with a thickness of 3 mm. It comprises 3 successive cylindrical parts, all of which have a diameter of 300 mm. and heights of 1 m., 1 m. and 1.5 m., respectively (from bottom to top).

In each of the two lower sections, cooling is effected by an axial cooler comprising an outer casing (having a diameter of 40 mm./44 mm. in the bottom section and 42 mm./48 mm. in the middle section) and an inner central passage comprising a tube with a diameter of 6 mm./10 mm., all these parts being made of stainless steel. Each cooling tube has a length of 1 m. and is supplied with distilled water by means of a metering pump. The gases are distributed through a sintered stainless steel plate at the base of the reactor.

The gases are freed from dust by means of an external cyclone fitted to the top section, the particles of catalyst collected being recycled through a stand-pipe to the bottom section, above the sintered distributor.

The feed mixture consists of a gaseous mixture of propylene, ammonia and water, together with air supplied by a compressor.

The isolation of the reaction products is effected by conventional cooling techniques, neutralisation with sulphuric acid and absorption of the neutral gas in water.

The catalyst is prepared in accordance with Example 6 of Belgian Patent Specification No. 622,025. This catalyst is obtained by precipitation, with ammonia, or iron and antimony salts, the Sb/Fe atomic ratio being 1.67/1. The catalyst has a particle size of between 40 and 150 microns.

Example 1

In the reactor described above, four tests were carried out:

(a) without filling elements;

(b) with baffles, each of which is made of a stainless steel plate with a thickness of 1 mm., perforated mechanically with staggered apertures with a diameter of 3 mm. These baffles are strung on the cooling tubes and fixed by spotwelding. Their spacing varies in dependence upon their number;

(c) with windings according to the present invention, made of stainless steel wire with a calibre of 2 mm., wound in turns with a diameter of 40 mm. and with a spacing of 10 mm. between turns, the length of each winding being 70 mm. These windings are stacked randomly in the reactor, the height of the stack being 175 cm.;

(d) with a mixed system comprising the use of windings of type (c) disposed between baffles of type (b).

89 litres of the antimony-iron catalyst described above is introduced in order to obtain a residence time of 4 seconds for a total flow per hour of 80 m^3 (n.t.p.) of the gaseous reagents. Under these conditions, the linear speed of this mixture is 31.4 cm./sec. The speed of entrainment of the catalyst is about 70 cm./sec. for the particle size used. The gas mixture fed to the reactor contains the following proportions of components, expressed in % by volume:

$$C_3H_6 : NH_3 : H_2O : \text{air} = 6 : 7 : 10 : 77.$$

The volume of the material of the windings constitutes 3.5% of the volume of the catalyst under working conditions. The temperature in the catalytic bed is, in each case, 450°C.

The following Table shows the influence exerted by the different filling systems on the results obtained:

TABLE

Tests	Eff.AN	Conv. C_3H_6	Productivity
(a) bed without fillings	40	60	51
(b) 7 baffles	50	79	64
10 baffles	53	80	68
16 baffles	54	88	69
(c) windings	60	93	76.5
(d) 5 baffles+windings	57	86	73

$$\text{Eff.AN} = \frac{\text{moles of acrylonitrile obtained}}{\text{moles of propene introduced}} \times 100$$

$$\text{Conv. } C_3H_6 = \frac{\text{moles of propene converted}}{\text{moles of propene introduced}} \times 100$$

Productivity=grammes of acrylonitrile produced per hour per litre of catalyst.

The above Table shows that, with the windings used according to the present invention (test c), better results are obtained than those obtained without windings (test a), by means of baffles (test b) or by a combination of baffles and windings (test d).

Example 2

With a charge of 56.5 litres of catalyst, a total flow of 90 m^3 (n.t.p.) per hour (residence time 2.26 sec., linear speed 35.4 cm./sec.), a volume of winding material constituting 5.6% of the volume of catalyst under working conditions and using a gaseous mixture comprising, as % by volume,

$$C_3H_6 : NH_3 : H_2O : \text{air} = 6 : 7.5 : 10 : 76.5,$$

the other conditions being those maintained in Example 1, the following results are obtained at 455°C.:

Eff.AN:	65%
Conv. C_3H_6:	95%
Productivity:	146

This Example shows that, by means of the process according to the present invention, it is possible for the residence time to be substantially reduced, thus making it possible to increase production considerably, while obtaining still better efficiency and conversion.

WHAT WE CLAIM IS:—

1. A process for carrying out chemical reactions, comprising passing at least one gaseous reactant through a fluidised bed of catalyst particles present in a reactor, said fluidised bed containing a plurality of filling elements therein to promote homogenity of the fluidised bed, and heat exchange means being provided which maintains the temperature of the fluidised bed at a desired value during the process, wherein the filling elements each consist of a winding of rigid material, the total volume of rigid material of said windings representing 2 to 12% of the total volume occupied by the said fluidised bed and the said rigid material and the speed of displacement of the gaseous reactant(s) through the fluidised bed in the reactor (as hereinbefore defined) is from 0.25 to 0.95 times the speed that would cause the entrainment of the particles of the fluidised bed of catalyst out of the reactor by the gaseous reactant(s).

2. A process according to claim 1, wherein the total volume of rigid material of the windings represents 3 to 10% of the total volume occupied by the fluidised bed and rigid material.

3. A process according to claim 1 or 2, wherein the speed of displacement of the gaseous reactant(s) through the fluidised bed is 0.40 to 0.90 times the speed which causes the entrainment of the particles of the fluidised bed of catalyst out of the reactor by the gaseous reactant(s).

4. A process according to any of the preceding claims, wherein the windings are formed of a wire having a diameter at least 0.4 mm.

5. A process according to any of the preceding claims, wherein the turns of the windings are separated from one another by a distance which is at least 20 times the dimension of the fluidised catalyst particles.

6. A process according to any of the preceding claims, wherein the diameter and length of the windings are such that at least two windings can be placed end to end over the minimum distance separating the walls of the heat exchange means.

7. A process according to any of the preceding claims, wherein the shape of the windings is such that interpenetration is negligible.

8. A process according to any of the preceding claims, wherein the shape of the turns of the windings is circular, oval or polygonal.

9. A process according to any of the preceding claims, wherein the windings are made from glass, a ceramic material or an inert or catalytically-active metal or metal alloy.

10. A process according to any of the preceding claims, whenever used for the synthesis of acrylonitrile from propylene, ammonia and oxygen.

11. A process according to claim 1 for carrying out chemical reactions, substantially as hereinbefore described and exemplified.

12. Products of chemical reactions, whenever carried out by the process according to any of claims 1 to 11.

VENNER, SHIPLEY & CO.,
Chartered Patent Agents,
Rugby Chambers,
2 Rugby Street,
London, WC1N 3QU.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.